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Two Critical Points for an Electron-Hole System

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Two successive phase separations can exist for an electron-hole system in a semiconductor having isoelectronic impurities within a certain density range: One is between bound excitons and a hole plasma with electrons pinned on the impurities, and the other one is between this hole plasma and the usual electron-hole plasma.

For some time, it has been speculated that the electron-hole (e-h) system in pure Ge could exhibit two critical points, one between a high-density and a low-density e-h plasma and one between the low-density e-h plasma and the exciton gas, the second one being induced by the Mott transition. But no experiment could be made supporting the existence of two such bumps in the e-h phase diagram.[1,2]

The purpose of this Letter is to show for the first time that two critical points can indeed exist for an e-h system if isoelectronic impurities are present in the material: When the density of impurities n_i lies in a certain range, the e-h system can undergo two successive phase separations, while for very low or very large n_i, there exists only one critical point. When the double phase separation exists, the first transition is between the usual electron-hole plasma (EHP) and a hole plasma (HP) with electrons pinned on the impurities, if the isoelectronic impurities are acceptorlike, while the second one is between this hole plasma and excitons.

Several experiments[3-5] have been done on GaP:N but up to now, no satisfactory explanation has been given of the exact role played by the impurities, when the density of electrons and holes is large. The physical picture of this problem, proposed in this Letter, should induce some more experimental work in order to prove the reality of these two critical points. In particular, arguments[3,4] have been given against the existence of a hole plasma in GaP:N on the basis that an electron is too light to be bound alone to the impurity; we will show that the answer is not as simple. First, electrons pinned on impurities polarize the HP and produce an ionic energy which increases with n_i and can stabilize the electrons enough to make the HP finally more stable than the EHP; second, the HP might not be the stablest state at $T=0$ but still appears at finite temperature.

In contrast to what happens for doped semiconductors, isoelectronic impurities will keep an equal amount of electrons and holes in the plasma as for a pure semiconductor. When a host atom is replaced by a lighter (heavier) one, there exists a short-range interaction between the impurity and the electron hole. For simplicity, we will consider only acceptorlike impurities. A bound exciton (BX) can be seen as an electron localized on the impurity and a hole bound by the long-range e-h Coulomb interaction.[6,7] When the impurity density n_i increases such that the distance between bound excitons goes below the Bohr radius, the exciton can no longer exist. One possibility is that the hole *and* the electron leave the impurity and form an EHP; another is that the e-h bond breaks but the electron stays localized on the impurity, the state being in that case the inverse of a metal: a hole plasma (HP) with negative ions.

Let us look at the energies of all these possible states of an e-h system.

(1) The free-exciton (FX) binding energy is $\epsilon_{FX} = -me^4/4h^2\epsilon^2$ if e and h have the same mass m. In the presence of an impurity potential, having a depth $U_0<0$ and a width d_0, one can find bound

excitons. For d_0 much smaller than the FX Bohr radius a_x, its binding energy is of order

$$\epsilon_{BX} \simeq 2\epsilon_{FX} + \epsilon_{ei}, \qquad (1)$$

where ϵ_{ei} is the energy needed to bind one electron to one impurity. ϵ_{ei}, estimated as $\epsilon_{ei} \sim U_0 + \hbar^2/2md_0^2$, can be positive or negative. One notes that for $0 < \epsilon_{ei} < -\epsilon_{FX}$, the impurity can bind an exciton but not an electron.

(2) Consider now an exciton with a density $n_i = (\frac{4}{3}\pi r_i^3)^{-1}$ of impurities with $d_0 \ll r_i$. This will not affect the BX energy if the average distance between BX is large and one neglects Van der Waals forces. The FX, having an electron delocalized in a volume V, gets from each of $n_i V$ impurities an energy $\sim U_0(\frac{4}{3}\pi d_0^3)/V$, so that its ground-state energy becomes

$$\epsilon_{FX}^{i} \sim \epsilon_{FX} + U_0(d_0/r_i)^3. \qquad (2)$$

(3) If the e and h form a plasma with density $n = (\frac{4}{3}\pi r^3)^{-1}$, each electron gets from the impurities about the same amount of energy[8] as FX, so the EHP average energy is

$$\epsilon_{eh}^{i}(n) \sim \epsilon_{eh}(r) + U_0(d_0/r_i)^3, \qquad (3)$$

where the EHP energy $\epsilon_{eh}(r)$ of the pure semiconductor is

$$\epsilon_{eh}(r) = \epsilon_e(r) + \epsilon_h(r) + \epsilon_{eh\,\mathrm{corr}}(r),$$

$\epsilon_e(\epsilon_h)$ being the energy of an e (h) gas and $\epsilon_{eh\,\mathrm{corr}}$ the contribution of the e-h correlations.

(4) Let us turn to the hole plasma. The energy of the holes in a jellium of negative charges is $\epsilon_h(r)$. It costs ϵ_{ei} to fix an electron on an impurity. If R_j are the positions of the electrons, the electrostatic energy of these pinned electrons in a jellium of positive charges is

$$E_{\mathrm{ion}} = \frac{1}{2}\int \frac{\tilde{\rho}(r)\tilde{\rho}(r')d^3r\,d^3r'}{|r - r'|} \qquad (4)$$

with $\tilde{\rho}(r) = -e\sum_j \delta(r - R_j) + ne$.

Moreover, these electrons on a jellium polarize the hole plasma and there results a polarization energy

$$E_{\mathrm{pol}} = \frac{1}{2}\int d^3r\,d^3r' \frac{d^3q}{(2\pi)^3}\exp[i\vec{q}\cdot(\vec{r} - \vec{r}\,')]\left(\frac{1}{\epsilon_q} - 1\right)\frac{1}{\epsilon_0 q^2}\tilde{\rho}(r)\tilde{\rho}(r'), \qquad (5)$$

where ϵ_q is the dielectric constant of the hole gas. E_{ion} cancels part of E_{pol}. Within the Thomas-Fermi approximation $\epsilon_q = 1 + q_0^2/q^2$, one obtains for N electrons and holes

$$N(\epsilon_{\mathrm{pol}} + \epsilon_{\mathrm{ion}}) \simeq -\frac{Ne^2 q_0}{2}\left(1 + \frac{4\pi n}{q_0^3} - \sum_{\vec{R}}\frac{\exp(-q_0 R)}{q_0 R}\right),$$

where the summation is taken on the vectors $\vec{R}$ which join one electron to the others. Note that the last two terms cannot be neglected when the average distance between electrons is not small compared to the screening length.

One finally gets, for the energy of a hole plasma with electrons pinned on impurities,

$$\epsilon_h^{i}(r) = \epsilon_h(r) + (\epsilon_{ei} + \epsilon_{\mathrm{ion}} + \epsilon_{\mathrm{pol}}).$$

The term in parentheses, which we call $\epsilon_{ei}(r)$, decreases with r: Even if ϵ_{ei} is positive, it is favorable to pin the electrons if n_i is large enough to allow negative values for $\epsilon_{ei}(r)$ (since $n \lesssim n_i$).

(5) If for $n = n_i$ the HP has a lower energy than the EHP, a minimum in the energy will exist at $n = n_i$; indeed for $n > n_i$, the extra electrons that cannot be pinned on impurities get instead of $\epsilon_{ei}(n_i)$ an energy $\epsilon_e(n - n_i) \sim 0$ for small $n - n_i$. If, moreover, n_i is not too large [compared to the minimum density n_0 of $\epsilon_{eh}(r)$], the energy of the EHP, which exists for $n \gg n_i$, will still have a minimum around n_0, so that finally the average energy $\epsilon(n, n_i)$ of the e-h system will show two minima.

What does this imply for the variation of the e-h phase diagram with n_i?

(a) For small n_i, $\epsilon_{ei}(n_i)$ is positive if $\epsilon_{ei} > 0$. The EHP energy will always be below that of the HP: The HP will never exist. If $\epsilon_{BX} > \epsilon_{eh}(n_0)$ one gets the usual phase separation between excitons and the EHP. This happens until $\epsilon_h^{i}(n_i) \sim \epsilon_{eh}^{i}(n_i)$.

(b) When n_i increases, one might have $\epsilon_{eh}^{i}(n_0) < \epsilon_h^{i}(n_i) < \epsilon_{eh}^{i}(n_i)$, i.e., the HP is not the stablest state, but it is stabler than the EHP at intermediate density. In such a case, the HP can only exist at finite temperature. For this to happen, one should compare the free energy $f_{eh}^{i}(h, T)$ of the EHP at n_0 and n_i with the free energy $f_h^{i}(n, T)$ of the HP at n_i. $f_{eh}^{i}(n, T)$ changes with T as $-C_{eh}(r)T^2/2$, the e-h specific heat being in the Sommerfield approximation

$$C_{eh}(r) = 2mk_F k^2/3\hbar^2 n = \alpha r^2. \qquad (6)$$

Since for equal e and h masses $C_{eh}(r) = 2C_h(r)$, $f_h^{i}(n_i, T)$ will decrease faster than $f_{eh}^{i}(n_0, T)$ if $r_i > r_0\sqrt{2}$. In that case, a phase separation between EHP and HP appears above a temperature T_T [which is roughly estimated by $f_{eh}^{i}(n_0 T_T)$

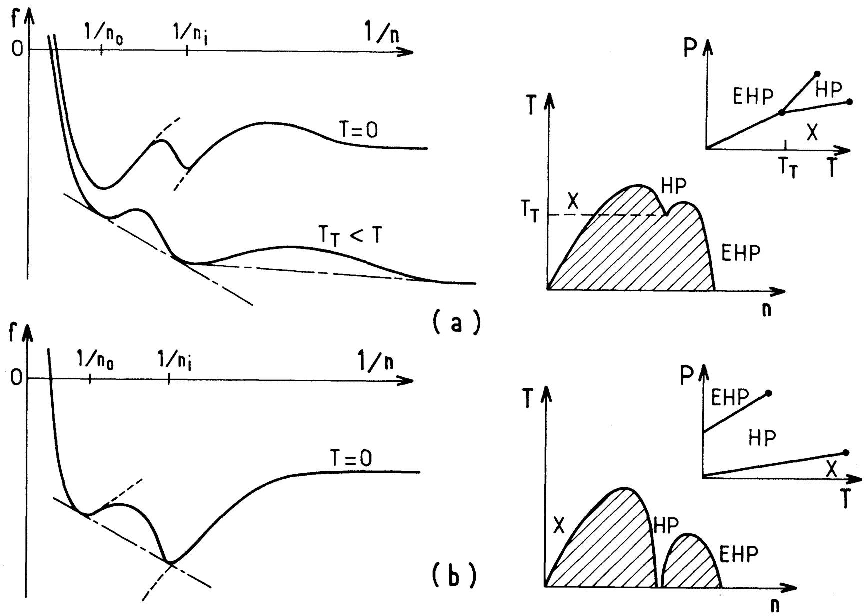

FIG. 1. The two possibilities for the HP-EHP phase separation, when the HP (a) is or (b) is not the stablest state.

$\sim f_h^i(n_i, T_T)$] if for n_i the HP has at T_T the lowest free energy [i.e., $f_h(n_i, n_i, T_T) < f_{eh}(n_i, n_i, T_T)$]. The resulting phase diagram [Fig. 1(a)] has two critical points.[9]

(c) For larger n_i, the hole plasma might become the stablest state. If n_i is still far from n_0, the e-h energy has two minima and an HP-EHP phase separation exists under pressure [Fig. 1(b)] at $T = 0$. For excitation n such that $\bar{n}_i < n < n_0$, the luminescence spectrum shows two plasmalike lines having the same high-energy edge (given by the unique chemical potential), the EHP one being wider than that of HP because $n_i < n_0$, so that its maximum is at lower energy although it is not the stablest state. Note that for $\bar{n} < n_i$, the phase transition between X and HP has a different chemical potential, so that the high-energy edge of the HP will rapidly decrease when $\bar{n}$ crosses n_i from above.

(d) For $n_i \gtrsim n_0$, ϵ can only have one minimum associated to a unique phase separation with one critical point between X and HP if HP is the stablest state at n_0.[10]

In conclusion, with increasing n_i, the phase diagram of an e-h system with isoelectronic impurities can go from (a) to (d), or skip state (c) and even state (b), depending on the material. This double phase separation is favored by a small ϵ_{ei} and a large n_0 (to allow large n_i).

Let us end by seeing if such new interesting phase diagrams (b) and (c) indeed exist. Indirect semiconductors in which isoelectronic traps produce bound states are, for example,[6] GaP:Bi and GaP:N. We will concentrate on the last one because experiments already exist which seem to support the existence of two critical points although more work would be highly desirable.

In GaP:N, values of free-exciton binding energy

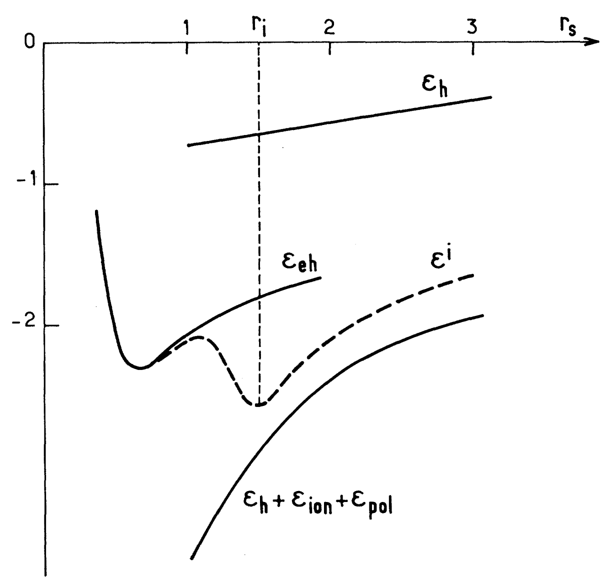

FIG. 2. Energies of a pure EHP (ϵ_{eh}), of a hole gas (ϵ_h), and of an e-h system (ϵ^i) in GaP:N when $r_i = 1.5$ and $\epsilon_{ei} = 4$ meV (the Rydberg unit is 13 meV and the Bohr radius 49 Å).

are quoted between 17 and 22 MeV.[11] The bound exciton is 11 meV below the free exciton so that ϵ_{BX} lies between 28 and 33 meV. The binding energy of the hole with respect to the charged impurity can be extracted from Cohen and Sturge[7] as 34 meV. [In the case of an ideal band structure, it corresponds to the term $2\epsilon_{FX}$ of Eq. (1).] This gives, for the energy ϵ_{ei} needed to bind the electron, values between 1 and 6 meV. The calculated energies[12] ϵ_h and ϵ_{eh} for a hole gas and an EHP in pure GaP are shown in Fig. 2, as well as $\epsilon_h + \epsilon_{ion} + \epsilon_{pol}$. $\epsilon_h^i(h)$ is obtained by shifting this last curve by ϵ_{ei}. One can then obtain the energy $\epsilon^i(n)$ of an e-h system in the presence of impurities by interpolating between the curve $\epsilon_h^i(n)$ up to n_i and $\epsilon_{eh}(n)$. In Fig. 2 we have shown as an example the curve $\epsilon^i(n)$ for $r_i = 1.5$ (effective Bohr radius 49 Å). We have used $\epsilon_{ei} = 4$ meV and neglected the difference between ϵ_{eh}^i and ϵ_{eh} (r_i being much larger than d_0). Therefore, we conclude that for such an impurity density, the hole plasma is the stablest state and the phase diagram is that of Fig. 1(b).

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[8]The short-range potential V_0 attracts the electrons and so polarizes the EHP. This leads to a second-order correction $\sim U_0^2(d_0/r_i)^3\, mr^2/\hbar^2$.

[9]One remarks that, for semiconductors with isoelectronic impurities, the Fisher rule of thumb (M. E. Fisher, private communication) is verified, which says that in order to have two critical points, one needs to have two distinct forces—here the impurity attractive force and the Coulomb force. This was not the case for the Mott transition.

[10]In fact, the EHP density increases slightly above n_0 when n_i increases.

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Origin of the Anomalous Enhancement of 180° Backscattering Yields for Light Ions in Solid Targets

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The origin of the enhancement of the near-surface yield of backscattered projectiles at angles close to 180° for swift light ions in solid targets is shown to be a correlation between outgoing and incoming paths which occurs when an ion scatters by almost 180° in one of its collisions in a solid. The theory does not invoke the crystal structure, or the disturbance of the medium by the ion. Calculations agree with experiment for 1-MeV He^{++} in Pt.

Recent measurements of scattering of H and He ions in amorphous and polycrystalline materials[1,2] have revealed a surprising enhancement of the near-surface yield at angles close to 180°. With the assumption of the usual proportionality of depth to energy loss, the results indicate that the intensity of scattered ions as a function of scattering angle θ, for a fixed depth $\lesssim 700$ Å, has a peak a few tenths of a degree wide at 180°.

We will show that the effect has the following simple explanation. In a case (such as shown schematically in Fig. 1) where a swift light ion scatters from a heavy atom through an angle 180°-α sufficiently close to 180° in a single collision, the outgoing path is, by time-reversal symmetry, nearly the same as the incoming one,[3] so that the

